

Adaptation of minerals processing operations for lithium-ion (LiBs) and nickel metal hydride (NiMH) batteries recycling: Critical review

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ARTICLE INFO

Article history:

Received 29 August 2012

Accepted 24 December 2012

Available online 27 February 2013

Keywords:

Recycling

Minerals processing

Lithium-ion batteries (LiBs)

Nickel metal hydride (NiMH) batteries

ABSTRACT

Production of LiBs and NiMH batteries is expected to increase rapidly due to the soaring price of oil and gas which increases interest in renewable energy as well as the introduction of hybrid vehicles (HVs), and electric vehicles (EVs) which used secondary batteries as an effective energy storage device. Development of an efficient recycling scheme to recover the valuable parts and safely dispose the harmful one at batteries end life is a necessity. The challenge, however, is how to recover all the valuable metals without sacrificing the economics of recycling process.

Several LiBs and NiMH batteries recycling processes have been developed in recent years. A review of these processes and their development timeline was presented in this paper. It was found that the major drawback of these recycling processes is the losses of some of batteries valuable parts since these recycling processes are not originally developed for this type of batteries. Also, some of these processes are expensive and designed for specific types of batteries which ignore contamination of recycling stream with impurities and other type of batteries.

Using minerals processing operations such as grinding, sieving, magnetic, electrostatic, and gravity separations to liberate batteries electrode materials and concentrate valuable metals is critical step in any recycling process. This may be due to the simplicity, efficiency, flexibility, and high throughput of these separation processes. The literature showed that applying these processes reduces the volume of LiBs and NiMH scrap, liberates their valuables, reduces the need for leachate purification in hydrometallurgical process, and facilitates the decomposing of battery's electrolyte. Based on these results a flowsheet to recycle mixed stream LiBs, and NiMH battery scrap was proposed.

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1. Introduction

Lithium-ion based batteries (LiBs) and nickel metal hydride (NiMH) batteries are currently dominated the portable electronics as well as hybrid vehicles (HVs) and electric vehicles (EVs) market. LiBs dominate the mobile phone and laptops industry while NiMH still shared large proportion of portable electronics such as camcorders as well as HV and EV. However, in recent years LiBs gradually replaced the NiMH batteries due to their higher volumetric and gravimetric energy density.

As an example, Japan secondary battery market statistics (Fig. 1) shows that LiBs market share increased linearly since its introduction to the market in 1993. In 2002, it had the same share as NiMH (about 30%) but since then it almost dominated the market with more than 65% share. On the other hand, NiMH batteries was representing 7.5% of Japan secondary battery in 1993. A peak value

(50%) was reached in 2000 but since then the share decreased drastically leaving it with just 22% in 2011 (Sullivan and Gains, 2010).

The main reasons for such increase can be summarized as follows (Dewulf et al., 2010; Lin et al., 2003; Zhang et al., 1998a):

1. Very good electrochemical properties of LiBs such as high energy density (120 W h/kg), high voltage (up to 3–6 V), longevity (500–1000 cycles), wide temperature range (−20 to 60 °C), and minimum memory effect.
2. LiBs do not contain hazardous heavy metals such as cadmium and lead.
3. Soaring price of oil and gas in recent years increasing the interest in renewable energy, HV, and EV which in turn increased the demand for secondary batteries in general as an effective energy storage device.

Some of batteries components are difficult to degrade. So discarding them after their end life into municipal waste may pollute the soil and underground water while their incineration contaminate the air by releasing toxic gases (Tedjar and Foudraz, 2010).

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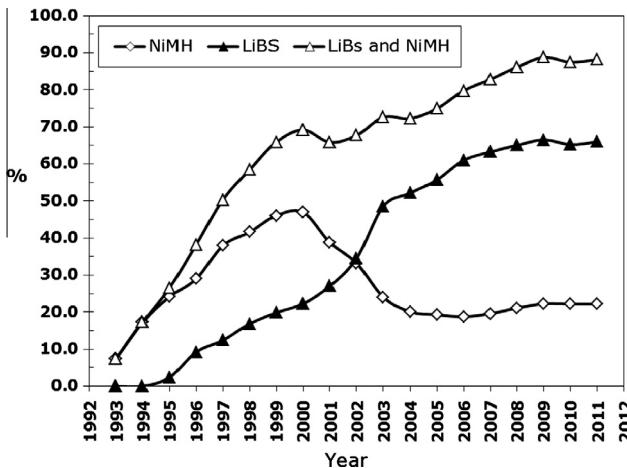


Fig. 1. LiBs and NiMH batteries share in Japan rechargeable batteries market (1992–2011) (Sullivan and Gains, 2010).

Also, the recent surge in minerals price encouraged battery recycling as a cheaper source of valuable metals (Ruffino et al., 2011). Therefore, the development of an efficient recycling scheme to recover the valuable parts and safely dispose the harmful one is a necessity. This is also encouraged by countries legislations which makes recycling free of charge for end users or by forcing the manufacturers to pay for it.

However, the amount of spent batteries available for recycling is small and does not match the large number of secondary cells produced for every year. For example, 97 tons of spent NiMH batteries were recycled in Germany in 2003 which represents only 3% of NiMH batteries produced in that year. According to Muller and Friedrich (2006), this may due to the following reasons:

1. Long life time of NiMH batteries (4–7 years) and the behavior of the end users who usually keeps spent batteries for another 2–4 years as "Hoarding time" before disposing them.
2. Inefficient spent batteries collection system either due to lack of legislations or public awareness.

Due to the heterogeneity of LiBs and NiMH batteries composition (Sections 2.1 and 2.2) as well as the spent batteries stream available for recycling, number of aspects need to be considered when designing an efficient recycling process. Firstly, designing recycling process for only one specific type of batteries is either technically difficult or economically unpractical. So the favorite choice is to develop a flexible recycling process (Castillo et al., 2002). Secondly, because of toxicity, reactivity, and corrosiveness of some components of these batteries, safe procedures are required during their recycling (MacLaughlin and Adams, 1999).

Self-ignition of spent NiMH batteries when they crushed due to the short circuit caused by moisture contact with hydrogen alloy powder is one aspect of safety risks. On the other hand, LiBs electrolyte (lithium phosphohexafluoride, LiPF_6) may react with water and produce toxic gases such as pentafluoro arsenic, pentafluoro phosphate, and hydrogen fluoride (Nan et al., 2006). Although LiBs used lithium ions instead of metallic lithium to reduce the risk of fire and releasing hydrogen gas, metallic lithium can be deposited on LiBs current collectors due to overcharging and discharging (Lin et al., 2003).

LiBs and NiMH batteries valuable or harmful components are tightly enclosed within battery case which usually made of steel, aluminum, plastics or nickel alloys. So, dismantling the outer shell by crushing and sieving removes the outer iron and plastic shell and facilitate the access to the valuable/harmful materials inside

spent batteries. This step is also reduces the scrap volume and improving the subsequent recycling processes such as fine grinding and magnetic separation. Once, the electroodal materials were exposed, ferrous and non-ferrous components can be extracted by pyrometallurgical or hydrometallurgical processes while plastics and papers can be either recycled or incinerated to generate power (Nan et al., 2006).

The aim of this paper is to review the use of physical separation processes such as crushing, grinding, classification, magnetic, electrostatic, and gravity separation in LiBs and NiMH batteries recycling. These processes are already established in minerals processing industry and they are characterized by their relatively low cost and flexibility to treat variable ores characteristics. Using such methods as a pretreatment step before using more expensive hydrometallurgical or pyrometallurgical processes will reduces the amount of impurities in these processes inputs which in turn reduces their cost and increases their selectivity.

In the first section, we gave a brief introduction about the structure of LiBs and NiMH batteries emphasizing the amount of valuable metals they contain while in the second section, a summary of the current recycling processes were given showing their advantages and timeline since their introduction to the market in early 1990s. Physical treatment of LiBs and NiMH batteries were thoroughly investigated in the third section. Data from literature was reanalyzed in order to attenuate the role of physical treatment on the liberation and separation efficiency of each component of LiBs and NiMH batteries. Economics of battery recycling were discussed in the fourth section while our conclusions and recommendations were presented in the fifth section.

2. Constituents of LiBs and NiMH batteries

2.1. LiBs

Different manufactures produce LiBs with variable components. So receiving variable spent LiBs structure is inevitable. This may affect the efficiency and cost of the current hydro-pyro-metallurgical based recycling processes.

In general, LiBs consist of positive and negative electrode, separator, electrolyte, and a stainless steel shell. Approximate percentage of each LiBs component is given in Fig. 2. The positive electrode consists of graphite coated on copper foil while the negative

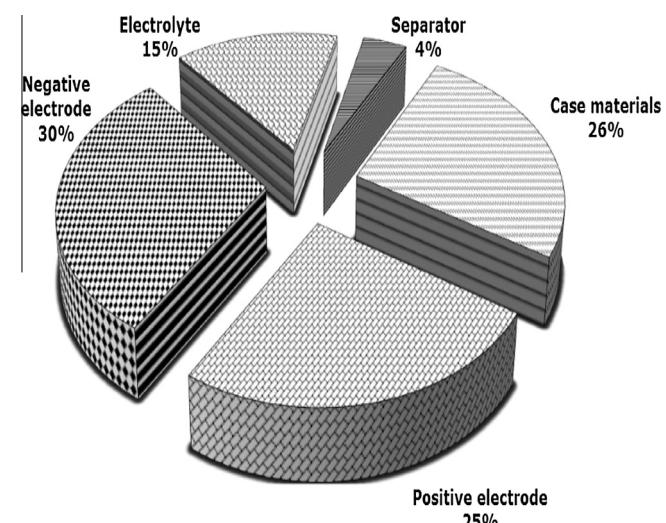


Fig. 2. LiBs major components (Georgi-Maschlera et al., 2012; Dewulf et al., 2010; Dewulf et al., 2008; Sullivan and Gains, 2010).

electrode is lithium mixed oxide such as LiCoO_2 , LiMn_2O_4 , and LiNiO_2 coated on aluminum foil. Both graphite and lithium mixed oxide powder are adhered to a supporting substrate by a polymer binder such as polyvinylidene fluoride (PVDF), butadiene-styrene copolymer, or modified cellulose. The Electrolyte is usually lithium salt such as LiPF_6 , LiBF_4 , LiClO_4 , and LiSO_2 solved in organic solvent such as ethylene carbonate (EC), propylene carbonate (PC) while the separator is made of micro porous polypropylene (PE) (Schmidt et al., 2003; Contestabile et al., 2001; Lin et al., 2003; Nan et al., 2006).

2.2. NiMH

NiMH batteries were launched in 1991 to replace hazardous cadmium containing batteries. Their positive electrode is nickel oxohydroxide (NiOOH) powder coated on a porous nickel substrate while the negative electrode is made of AB5-hydrogen storage alloy powder (Mischi metal-Ni-Co) coated on iron or copper plate. The cathode and anode are separated by an inert separator made of nylon (polyamide) or polypropylene while the electrolyte is made of potassium hydroxide (KOH) or sodium hydroxide (NaOH) solution (Fig. 3). The main Rare Earth Elements (REEs) in the (Mischi metal-Ni-Co) alloy are lanthanum (La), praseodymium (Pr), neodymium (Nd), samarium (Sm), and cerium (Ce) (Muller and Friedrich, 2006; Zhang et al., 1998b; Nan et al., 2006).

3. State of the art in battery recycling technology

3.1. The importance of LiBs and NiMH batteries recycling

Besides the environmental benefits of LiBs and NiMH batteries recycling, they become possible cheaper source for metals due to the recent surge in minerals prices. As shown in Fig. 4, the main metals in LiBs scrap are cobalt, nickel, lithium, copper, manganese, and iron/steel while NiMH batteries contain nickel, cobalt, zinc, manganese, iron/steel as well as REE such as lanthanum, neodymium, cerium, praseodymium, and samarium. Usually, metals are recovered in their metallic form while lithium as lithium carbonate. Although economical attractiveness and environmental necessity; the challenge in battery recycling is how to recover all the valuable metals without sacrificing the economics of recycling process (Nan et al., 2006).

Dewulf et al. (2010) used “Exergy” method to quantify the savings in minerals resources if LiBs cathode active material is solely

made of recycled spent batteries by comparing two scenarios. One scenario is when (LiMeO_2 , Me: Co, Ni, Mn) is manufactured by using cobalt and nickel from natural (virgin) resources while the second scenario is when recycled cobalt and nickel are reused in active material manufacturing. Manganese ore is used in both scenarios since no major manganese recycling technology is currently available.

“Exergy” method is based on second law of thermodynamics which states that “if no energy enters or leaves a given system from the surrounding environment, the potential energy of the system in its new state will always be less than that of initial state”. Since some of the system energy is dissipated to the environment as heat and cannot be reversible, “Exergy” terminology is used to refer to the useful energy of the system which can do work (i.e. reversible) when reached equilibrium with its surrounding. Exergy value of each product is calculated from the value of its components while the cumulative input and output Exergy of a given system/industrial process is calculated from the Exergy of its inputs and outputs. This enables the quantification and modeling of input-output relationship of any industrial system (Dewulf et al., 2010; Dewulf et al., 2008). According to Dewulf et al. (2010), if only recycled cobalt and nickel are used in the production of LiBs cathode active materials, the following savings can be achieved, 51.3% in natural resources, 45.3% in fossil fuel resources, and 57.2% in nuclear energy demand.

In recent years, countries strengthen their battery recycling regulations which encouraged the development of economic and flexible recycling processes aiming at ensuring the availability of accessible collection points to enable the end users to discard their spent batteries with no cost. For example, EU regulations required that each member state is obliged to reach 15–25% minimum collection rate for spent batteries and accumulators by 2015 with at least 45–50% recycling efficiency. Incineration of batteries to generate energy is not included in the efficiency calculation which means that any recycling process should consider the recovery of all materials and not only the metals in order to reach this target. In some countries such as Germany it is compulsory for batteries producers and importers to collect spent batteries from the end users and recycle them according to the environmental regulations paying for the cost of all recycling process including collection, processing, and disposal (Georgi-Maschlera et al., 2012; Granata et al., 2012; Muller and Friedrich, 2006).

3.2. Current recycling technologies

In general, current recycling technologies for LiBs and NiMH batteries can be divided into two broad categories (Dewulf et al., 2008):

- Physical based technologies.
- Chemical based technologies.

The main subcategories of physical separation technologies are gravity, magnetic, electrostatic based separations, while chemical based technology includes leaching, bioleaching, solvent extraction, precipitation, and electrolysis based separations. pyrometallurgy and mechanochemical separations can be categorized as chemical based separations. In the following sections, a brief review of these technologies will be given emphasizing their timeline and major breakthroughs. However, for more details of these recycling processes, the reader may refer to Bernardes et al. (2004), Espinosa et al. (2004), Castillo et al. (2002) and Xu et al. (2008).

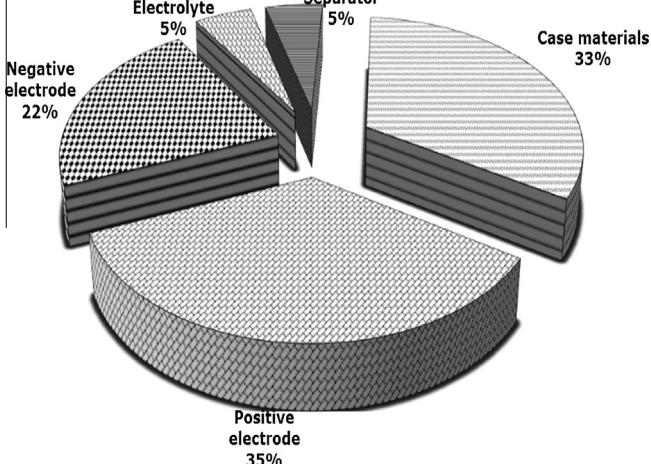


Fig. 3. NiMH battery major components (Zhang et al., 1998b; Vassura et al., 2009; Huang et al., 2011; Sullivan and Gains, 2010).

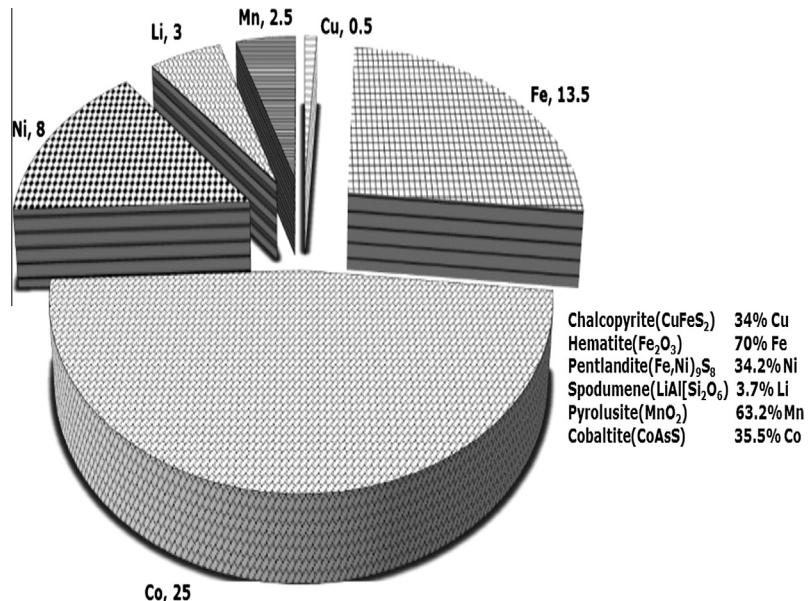


Fig. 4. Elemental analysis (wt%) of LiBs battery in comparison with common metal ores (Granata et al., 2012; Vassura et al., 2009; Dewulf et al., 2010).

3.3. Hydrometallurgical process

Hydrometallurgical processes require dissolving metals from spent batteries scrap and then selectively separate them from the leach liquor. One of the early developed LiBs recycling processes is Toxco's process (MacLaughlin and Adams, 1999; MacLaughlin, 1994). It includes submerging spent batteries in liquid nitrogen to deactivate them. Then the frozen batteries were crushed and placed in aqueous solution with high pH controlled by lithium hydroxide (LiOH). Different lithium salts (LiCl, Li₂CO₃ and LiSO₄) were precipitated, filtered, and then washed with mild sulfuric acid (H₂SO₄). Finally lithium carbonate (Li₂CO₃) was formed by pumping CO₂ into the solution.

Another hydrometallurgical process is Recupyl process which used hydrolysis to recover the valuable from mixed spent LiBs (Tedjar and Foudraz, 2010). Fine powder (−3 mm) prepared from spent batteries scrap by crushing, magnetic separation, followed by densimetric table, were subjected to high turbulent hydrolysis. Carbon dioxide saturated water was finally used to wash the powder in order to form lithium carbonate.

Kawakami (1999) recycling process was originally developed for lithium metallic containing batteries. Even though these types of batteries have been abandoned because of safety concern, some aspects of this recycling process can be used in LiBs recycling. In Kawakami process, spent batteries were cut by water jet (>3.50 KPa) in sealed container filled with inert gas (argon) to prevent ignition by cutting sparks and evolving hydrogen when lithium react with water. Hydrogen released from the cutting process is collected and reused while lithium hydroxide is separated from the solution by precipitation, filtration, and drying. An organic solvent (methyl alcohol) is added to the solution to precipitate the remaining lithium hydroxide while the solid residues were pulverized which can be recycled by standard procedures. The remaining solution is purified from unrecyclable polymers by burning at high temperature.

Zhang et al. (1998a) developed a hydrometallurgical technology to recover cobalt and lithium from spent LiBs. The spent batteries were manually shredded and the anode materials were separated. Then, anode materials were leached with hot hydrochloric acid where cobalt is extracted from the solution by PC-88A. The raffinate was concentrated by evaporation before lithium carbonate

is precipitated by adding saturated solution of sodium carbonate (NaCO₃).

Hsinch process (Lin et al., 2003) used membrane hydrolysis in LiBs recycling. Firstly, spent batteries were punched, calcined (500–800 °C) to decompose the electrolyte, and crushed to fine powder (−3.35 mm). Secondly, the powder (−300 µm) rich in valuable metals (Co and Li) was separated from metal scrap which mainly contains iron, aluminum, and copper foil. The coarse fraction was subjected to magnetic separation to separate magnetic from nonmagnetic materials. The non-magnetic part was subjected to Eddy current separator to separate copper from aluminum. On the other hand the electroodal powder (−300 µm) were digested in hot hydrochloric acid and sodium chloride. After removing the remaining carbon by precipitation, a membrane electrolysis cell with a cathode consists of spent batteries and hydrochloric solution and anode made of brine were used to form copper on the cathode surface while hydrogen ions formed in anode solution pass the membrane and form hydrochloric acid in cathode solution. Once hydrolysis process is completed, hydrochloric acid can be recovered from the cathode solution by dialysis treatment. Another membrane hydrolysis (second cell but with different current density) were used to deposit cobalt on cathode surface. Then the remaining solution were further purified from iron and aluminum by adjusting pH in order to precipitate aluminum and iron hydroxide where they separated by filtration, finally, sodium carbonate was added to the filtrate to precipitate lithium carbonate.

Zhang et al. (1998b) developed hydrometallurgical process to recycle NiMH batteries. The spent batteries were manually cut to remove the case and expose the electroodal material. Then the electroodal powder was leached by hot hydrochloric acid and the Rare Earth Elements (REEs) were extracted from the leach liquor by the solvent extraction (D₂EHPA). After stripping REE by hydrochloric acid, they were precipitated as oxalates from their impurities. On the other hand, cobalt were extracted by the solvent extraction TOA (triethyl amine) and precipitated as oxalate while Ni is directly precipitated from the leach liquor by ammonium oxalate.

Pietrelli et al. (2002) used sulfuric acid to leach REE from crushed NiMH batteries then precipitated them as insoluble Na-REE double salts by adjusting pH and addition of sodium hydroxide. AEA technology (Lain, 2001) requires grinding spent

LiBs in inert and dry atmosphere. Then the electrolyte is recovered by immersing the crushed spent batteries in anhydrous solvent with boiling temperature less than the decomposition temperature (80 °C) of the electrolyte. After extracting the electrolyte, the scrap is immersed in warm (50 °C) solvent in order to dissolve the binder (PVDF) and free the electroodal materials from their supporting substrate. The electroodal powder is then filtered from the solution and subjected to electrochemical reduction in order to reduce copper (+3) to copper (+2) which forms insoluble cupric oxide and aqueous lithium hydroxide.

Ra and Han (2006) used Etoile–Rebatt technology to recycle LiCoO₂ from LiBs scrap. The process includes the dissolution of spent electroodal materials then an electric current was used to precipitate the dissolved LiCoO₂ on a platinum electrode.

Mishra et al. (2008) used a bio-hydrometallurgical process to recycle spent LiBs. They used Acidithiobacillus Ferrooxidans (ATCC19859) bacteria to leach cathode waste powder (−150 µm) in presence of sulfur and iron in ferrous state. ATCC bacteria metabolize the sulfur and produce sulfuric acid which dissolves the cobalt and lithium from LiBs cathode powder.

3.4. Pyrometallurgical processes

Inmetco process was not originally developed for battery recycling. In this process, LiBs and NiMH spent batteries are fed as a secondary charge with iron-containing materials in order to produce iron-based alloys. Copper and nickel were recovered while other metals were slagged. Carbon and organic materials were burnt and utilized as reducing agent (Georgi-Maschlara et al., 2012).

Also, NiMH batteries were recycled as a feed in stainless steel production. But in this case cobalt and REE were slagged and lost (Muller and Friedrich, 2006). On the other hand Kayser–Umicore process (Georgi-Maschlara et al., 2012) used spent LiBs and NiMH batteries as a furnace secondary charge. Nickel and cobalt were recovered while other materials were either slagged, or used as reducing agent or energy source.

IME process was developed to recycle NiMH batteries. Spent batteries were firstly crushed and sieved to remove iron and plastic, then the crushed battery scrap was melted in electric arc furnace to produce Ni–Co alloy. Manganese, iron, aluminum, and carbon were removed by selective oxidation at temperature 1600 °C. The slag which is rich of REE's (50–60 wt%) was chemically treated to recover the REE (Muller and Friedrich, 2006).

Generally, reductive roasting is an effective and safe method for LiBs recycling. It enables cobalt recovery but it is accompanied by generating toxic HF gasses. Also, lithium-containing slag can be used in cement and concrete industry (Saeki et al., 2004; Ziemann et al., 2012).

Sumitomo–Sony (Cardarelli and Dubi, 2007) is one of the early processes dedicated for LiBs recycling. It was developed by collaboration between Sony and Sumitomo metal mining to recycle LiBs batteries used in Sony electronics. Spent batteries were calcined to remove electrolyte and plastics, and then the remaining scrap was pyrometallurgically treated to recover Co–Ni–Fe alloy then the cobalt was hydrometallurgically separated from the alloy in order to reuse it in manufacturing new batteries. Copper and stainless steel were physically separated as by product while lithium and other valuable metals were lost in the slag.

In order to recover LiBs electrolyte, Schmidt et al. (2003) developed a process to recycle electroodal materials (positive and negative electrode, electrolyte and the separator) from spent LiBs in order to reuse them for manufacturing new batteries. After removing the battery case, the electroodal materials were crushed in dry ethyl acetate (water < 50 ppm) and kept for at least 5 h in order to extract the electrolyte and soften them. Then the spent batteries

were further ground to separate negative and positive electrode from the remaining electrolyte. The negative electrode was kept in dry ethyl acetate for 8 h where the electrolyte (lithium salt and its solvents) as well as the binder were extracted by ethyl acetate solvent. Finally the negative electrode material was dried, pulverized, and subjected to high-temperature treatment.

Chen et al. (2011) suggested the use of vacuum-aided pyrometallurgy to recover metallic cobalt and Li₂O from LiBs spent batteries scrap. The process includes the decomposition and reduction of LiCoO₂ at high temperature (700 °C) and carbon to CaO then to metallic cobalt.

3.5. Hydro-pyrometallurgical processes

Umicore process was designed for LiBs and NiMH battery recycling. The spent battery feed is charged directly into specially designed furnace where cobalt and nickel were recovered as Co(OH)₂/CoCl₂ and Ni(OH)₂, respectively. Copper, zinc, manganese, and iron were recovered in aqueous solution while carbon and organic materials were burned and used as reducing agents. CoCl₂ was then used to manufacture LiCoO₂ (Umicore, 2010; Sullivan et al., 2011).

IME (LiBs) process consists of manual LiBs sorting and dismantling to remove the outer case and electric components. The batteries were then retorted at 250 °C to deactivate them and to remove the volatile electrolyte as condensate. Two fractions, coarse (+200 µm) rich of iron and nickel, and fine (−200 µm) rich of aluminum and electroodal materials were separated by crushing, sieving, magnetic separation, and zigzag classifier. The fine fraction was pelletized and pyrometallurgically treated by electric arc furnace to produce cobalt alloys while the flue dust and slag were leached with sulfuric acid to produce lithium carbonate (Georgi-Maschlara et al., 2012).

Granata et al. (2012) developed hydro-pyrometallurgical process to recycle spent LiBs where spent batteries are firstly crushed and sieved to (−1 mm) particle size. The coarse fraction (+1000 µm) were retorted (300 °C) and then subjected to Eddy current separator to separate ferrous, nonferrous, and nonmetals. The fine fraction (−1000 µm) were leached by mixture of sulfuric and hydrochloric acid. Then iron and aluminum were removed by precipitation while cobalt and nickel were separated by solvent extraction (Cyanex 272).

Also, Granata et al. (2012) developed hydro-pyrometallurgical process to recycle spent NiMH batteries. Similar to LiBs, spent NiMH batteries were crushed and sieved to (−1 mm) sieve size. The coarse fraction was then retorted (300 °C) and subjected to Eddy current separator to separate ferrous, nonferrous, and nonmetals. The fine fraction was leached by mixture of sulfuric and hydrochloric acid. Iron and aluminum were removed by precipitation while manganese was firstly separated by solvent extraction (D₂EHPA) followed by cobalt while the nickel was extracted by Cyanex 272.

Cirimat process is a hydro-pyrometallurgical process for LiBs recycling. It includes digestion of the electroodal materials with hot nitric and sulfuric acid then selective precipitation was used to precipitate lithium and manganese as metal hydroxides. The remaining solid is incinerated in a muffle furnace at (500 °C) to remove carbon, organic materials, and producing metal alloy (Castillo et al., 2002).

Contestabile et al. (2001) developed a laboratory scale hydro-pyrometallurgical process to recycle spent LiBs. The electroodal materials were liberated by crushing and grinding, and then hot N-methylpyrrolidene (NMP) was used to dissolve the binder and liberate active materials from their supporting substrate. The powder was then leached with hydrochloride acid where cobalt was precipitated as cobalt hydroxide by adjusting solution pH.

3.6. Recycling mixed types of spent batteries

As mentioned earlier, due to the behavior of end-users, the variability in manufacturers specifications, and the economics and efficiency of automatic sorting process for a real stream battery waste, it is inevitable that different type of batteries and accumulators are mixed within waste stream. In some cases mixing battery waste may have some advantages: for example mixed LiBs and NiMH waste neutralize the solution since spent LiBs produce acidic media while NiMH batteries produce corrosive alkaline solution (Nan et al., 2006).

Bartec is one of the recycling processes developed to recycle mixed type of batteries. It includes crushing the spent batteries in CO_2 gas atmosphere to liberate battery component and remove the volatile electrolyte as condensate (Georgi-Maschlera et al., 2012). Also, EcoBat process was developed to recycle mixed types of LiBs and NiMH scrap. It employed mechanical separation to dismantle the anode and cathode materials for each type of batteries then used supercritical CO_2 to extract LiBs electrolyte (Sullivan et al., 2011)

Granata et al. (2012) developed a hydro-pyrometallurgical process for a real upstream spent batteries scrap containing 20% LiBs, 40% NiMH, and 40% primary lithium batteries (PLBs). Spent batteries were firstly deactivated by retorting at 300 °C and then crushed and sieved to (-1 mm) sieve size. The coarse fraction ($+1000\text{ }\mu\text{m}$) which mainly contains metals was subjected to Eddy current separator to separate ferrous and nonferrous metals from nonmetal fractions. The fine fraction ($-1000\text{ }\mu\text{m}$) were leached by a mixture of hydrochloric and nitric acid then metals (nickel, cobalt, and aluminum) were separated by solvent extraction.

Nan et al. (2006) developed a process to recycle LiBs and NiMH batteries. Firstly each type of batteries was dismantled separately and the case material and electrolyte were removed. Then LiBs scrap was leached by sodium hydroxide in order to remove the alumina foil while the remaining scrap was heated in a furnace (600 °C) to burn organic, plastic and the remaining electrolyte. On the other hand, NiMH batteries scrap were also heated in a furnace (600 °C) to burn organic and plastic, then sieved to (-1.5 mm) to separate the remaining iron shells. Mixed powder from NiMH and LiBs were leached by sulfuric acid and hydrogen peroxide. Then, REE elements were precipitated and separated from the solution by adjusting its pH by a mixture of NaOH and Na_2CO_3 . Solvent extractor (Acorga M5640) was used to extract the copper from the filtrate whereas the cobalt and nickel were extracted by Cyanex 272 at different pH.

3.7. Recycling of other Li-containing batteries

New types of Li-ion based batteries are continuously introduced to the market aiming at improving gravimetric and volumetric electrochemical properties of existing cells. $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, LiFePO_4 , LiMnO_4 , $\text{LiMnO}_4/\text{LiTiO}_{12}$, and Li-polymer batteries are some of the secondary batteries available in the market. So taking into account these new contaminates in spent battery waste stream is justified especially with increased demand on HEV and EV.

Lithium metal polymer rechargeable batteries (LMPBs) which are characterized by their high energy density are mainly used in hybrid (HV), electric vehicles (EVs), and electric power storage. They consists of anode, cathode, and electrolyte similar to standard LiBs batteries but their cathode is made of lithium vanadium oxide and carbon powder coated on a thin aluminum foil while the anode is made of ultra-thin lithium metal foil. The electrolyte is made of a solid copolymer containing lithium salt. These types of batteries are highly reactive and expensive, so their recycling is very

important from economic and environmental standpoint (Cardarelli and Dubi, 2007).

Cardarelli and Dubi (2007) developed a novel method to recycle LMPB batteries. Firstly, the spent LMPB were dismantled to remove the case and electric hardware, then they were frozen ($-180\text{ }^\circ\text{C}$) to soften the polymer/solid gel and deactivate them. The frozen spent batteries were comminuted in an inert environment such as liquid argon to ($-1000\text{ }\mu\text{m}$). The slurry was then incinerated ($700\text{ }^\circ\text{C}$, 1000 KPa) for 8 h to evaporate argon. The remaining spent batteries scrap which is free of carbonaceous materials and consists mainly of metals and metal oxides as well as the purified dust from incineration process were digested with hot sulfuric acid. The vanadium was oxidized by oxidizing agent and separated from the mother liquor as hydrated vanadium oxide by adjusting pH followed by precipitation and filtration. The remaining filtrate were purified from heavy metals by electrophoretic deposition (EPS) and concentrated by evaporation whereas aluminum was precipitated and filtered as aluminum hydroxide by adding ammonia and adjusting solution pH leaving the final solution with purified lithium sulfate.

4. Drawbacks of current recycling technologies

In view of previous discussions, the main concerns of secondary battery recycling are safety and cost. Lithium ion batteries may blow up during recycling due to the rapid oxidation of lithium metallic which may be deposited due to battery overcharging. Therefore, pretreatment of this type of batteries either thermally or cryogenically is a necessity for safety reasons (Shin et al., 2005). Also, LiBs contains toxic LiPF_6 electrolyte while NiMH batteries contains corrosive alkaline electrolyte, so special arrangement need to be taken to deal with these toxic materials which increase the cost of any recycling process (Nan et al., 2006). Taking into account the safety issues, the major drawbacks of current recycling technologies can be summarized as follows:

- Most of recycling processes were not originally developed for LiBs or NiMH batteries so some of the batteries valuable parts cannot be recovered. For example, lithium is lost in Inmetco and Kayser-Umicore recycling processes (Georgi-Maschlera et al., 2012).
- Most of hydrometallurgical based recycling processes were developed for specific type of batteries, e.g. LiBs or NiMH batteries. These processes were developed in laboratory scale with manual sorting and dismantling. Therefore, they ignore the inevitable diversity of real spent batteries stream which may contain mixture of spent batteries including lithium primary batteries which contain metallic lithium and manganese. LiBs active cathode material is not always pure LiCoO_2 but it may contains other structures of active materials such as: $\text{LiCo}_{1-x}\text{Sn}_x\text{O}_2$, $\text{LiCo}_{1-x}\text{Mg}_x\text{O}_2$ and $\text{Li}(\text{MnNiCo})\text{O}_2$. So designing a recycling process for each type of cathode active material is not practical in terms of commercial point of view (Xu et al., 2008).
- Usually electrolyte, plastics, and organic were burnt or evaporated by pyrometallurgical recycling process. However some recycling process claimed that electrolyte can be recovered as condensate during battery calcination. When LiBs were thermally treated before crushing and sieving the weight loss was 34.51% of the spent battery original weight while when they firstly crushed and sieve to separate the fine part and only incinerate the coarse part ($+1000\text{ }\mu\text{m}$), the losses was just 5% (Georgi-Maschlera et al., 2012; Granata et al., 2012). IME process (Georgi-Maschlera et al., 2012) claimed 80% electrolyte organic solvent (70% ethyl methyl carbonate, 10% ethylene carbonate) recovery as condensate from pre-treatment process.

- The presence of impurities affects the efficiency of both hydrometallurgical and pyrometallurgical processes. For example, the presence of carbon affects the efficiency of pyrometallurgical process. Georgi-Maschlera et al. (2012) reported that it was required to pre-treat electric arc furnace feed in a rotary kiln at 800 °C in order to reduce its graphite content from 30% to 15% weight. Also, the presence of manganese (Mn) affects the efficiency of producing acceptable quality cobalt alloy per metallurgical process. Moreover, Pietrelli et al. (2002) reported that the presence of iron may cause difficulties in separation Co, Ni, Zn by ion exchange and solvent extraction from NiMH battery scrap. Ito et al. (2010) reported that physical separation is required to separate Co and REE from NiMH scrap before recovering Ni by direct smelting. Therefore, the current pyrometallurgical LiBs recycling technologies may not applicable to other type of LiBs such as LiMnO₂. Granata et al. (2012) reported that even low manganese concentration such as 3 g/L significantly reduced selective separation of cobalt by Cyanex 272.
- The economics of hydrometallurgical process is sometimes questionable, low solid concentration is required for high leaching efficiency which may reduce the process throughput. Shin et al. (2005) mentioned that increasing solid concentration from 50 to 100 g/L in 2 M sulfuric acid decreased the leaching efficiency by 30–35%. Even though hydrometallurgical recycling requires high concentration of acid at high temperature (70–80 °C), some valuable metals such as cobalt are not completely leached (80% maximum recovery) (Saeki et al., 2004). Moreover, contamination of lithium during recycling process may affect the quality of the final product or make the recycling process economically less attractive (MacLaughlin and Adams, 1999).
- Some spent batteries components cannot be leached easily. The binder (PVDF) is a strong adhesive which cannot be dissolved by most of strong acids, and organic reagents at room temperature (Dewulf et al., 2008). For example, lithium cobalt oxide does not leach easily with commonly used leachants due to the strong bond between oxygen and cobalt (Shin et al., 2005). Leaching agents such as hydrogen peroxide (H₂O₂) causing the reduction of Co(III) to Co(II); this facilitate cobalt leaching but increases the cost of the hydrometallurgical process. Therefore, regeneration (renovation) of lithium cobalt oxide from battery waste and reused it will be more advantageous from economic point of view. Also, PVDF and the remaining carbon did not dissolve in acid leaching but float at the surface of leach liquor which requires filtration (Shin et al., 2005). However, some researchers such as Castillo et al. (2002) suggested leaching the spent batteries by using hot (100 °C) N-methyl2-pyrrolidone (NMP) for 1 h as pretreatment in order to liberate active materials from their supporting substrate. However, some reported that PVDF can be partially dissolved in some ethers, ketones, and oleum (Xu et al., 2008).
- Because of heterogeneous composition of LiBs and NiMH batteries, Single recycling process is only able to extract specific part of battery components. So a combination of recycling process is required in order to efficiently extract all battery components. Lithium cannot be recovered by pyrometallurgical process alone, so a combination of hydro and pyrometallurgical process is required. However, using hydrometallurgical process to leach lithium after using pyrometallurgical process require grinding slag ($P_{95} = 100 \mu\text{m}$) which means extra cost of recycling process (Xu et al., 2008; Georgi-Maschlera et al., 2012).

5. Mechanical treatment of LiBs and NiMH batteries

In minerals processing, grinding is a necessary step prior to any separation process aiming at liberating valuable particles from

gangue. Spent batteries, therefore, require crushing and grinding in order to liberate electroodal materials which are encapsulated in iron and plastic case. Many researchers emphasized the importance of mechanical treatments of spent batteries as a prerequisite for hydrometallurgical process. Mechanical treatment is characterized by its simplicity, efficiency, flexibility, and high throughput; however, it consumes considerable amount of energy (Huang et al., 2011).

Due to spent batteries heterogeneity, primary crushing requires high speed crushers with high reduction ratio (10–15:1) in order to liberate their components. Active materials in spent batteries electrodes are made of fine powder which requires extintive grinding to liberate them from their supporting substrates; for example, particle size of LiCoO₂ in reagent grade is about 10–15 μm (Saeki et al., 2004; Ruffino et al., 2011).

After liberation of battery components, valuable components were concentrated using standard minerals processing operations such as magnetic, electrostatic, and gravity separations. Using other minerals processing operations such as flotation in concentrated battery components is limited. Chen et al. (2011) reported that Jin et al. (in Chinese) used a non-ionic collector (kerosene) to separate carbon and LiCoO₂ from spent LiBs powder ($-200 \mu\text{m}$). They reported high purity LiCoO₂ (93%) and high recovery (92%). However, the recovered LiCoO₂ need to further purified in order to use it battery manufacturing. Another related work is the work of Ogguniyi and Vermaak (2009) for recycling printed circuit board (PCB) fines. Samples of PCB fines ($-75 \mu\text{m}$) were subjected to froth flotation in 3.5 L flotation cell without the addition of any reagents (collector and frother) but at various flotation parameters such as air flow rate, pulp density, and impeller rotational speed. According to the authors, stable froths were formed at the top of the cell which indicates that natural hydrophobic response exists. Many of the metallic elements were found to concentrate into the sink. Gold (Au) was among the elements best enriched with approximately 64% recovery at 2 enrichment ratio 3.1 (676 ppm actual assay).

Also, the work of Hirajima et al. (2005) on the use of froth flotation to separate rare earth phosphorus from waste fluorescent lamps may be beneficial in upgrading spent LiBs. The authors used dodecyl ammonium acetate (DAA) as cationic collector, sodium dodecyl sulfate (SDS) and sodium oleate (NaOl) as anionic collector, and sodium silicate (Na₂SiO₃) as dispersant. The authors reported 70–90% recovery and 0.26–0.37 Newton's efficiency of rare earth phosphorus from actual discarded waste lamp.

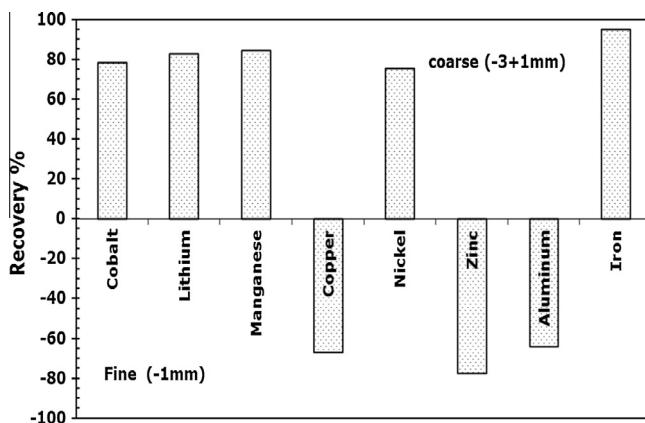


Fig. 5. Recovery of valuable metals from spent LiBs scrap by grinding and sieving (Vassura et al., 2009).

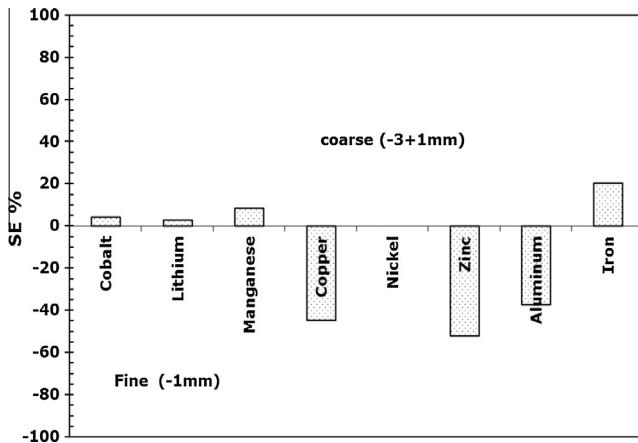


Fig. 6. Separation efficiency (SE) of valuable metals from spent LiBs scrap by grinding and sieving (Vassura et al., 2009).

5.1. Mechanical treatment of LiBs

Mechanical treatment of spent LiBs batteries improves the concentration of metals which reduces the need for leachate purification in hydrometallurgical process. Also, crushing facilitates the decomposing of the electrolyte (LiPF_6) into lithium fluoride salt (LiF) and the soluble phosphorous pentafluoride (PF_5) as well as evaporating the organic solvents propylene carbonate (PC) and diethyl carbonate (DEC) which improves lithium recovery (Xu et al., 2008; Shin et al., 2005). Figs. 5 and 6 show that primary crushing followed by sieving concentrated valuable metals in both coarse and fine fractions. Recovery and separation efficiency were calculated by Eqs. (1) and (2). However, the separation of valuable metals was not completed due to inefficient liberation.

$$\text{Recovery} (\%) = \frac{\text{coarse} \times [\text{feed} - \text{fine}]}{\text{feed} \times [\text{coarse} - \text{fine}]} \quad (1)$$

$S.E(\%) = \text{Recovery of valuable to coarse fraction}$
 $- \text{Recovery of none valuable to coarse fraction}$

$$S.E(\%) = \frac{[\text{feed} - \text{fine}] \times [\text{coarse} - \text{feed}]}{\text{feed} \times [1 - \text{feed}] \times [\text{coarse} - \text{fine}]} \quad (2)$$

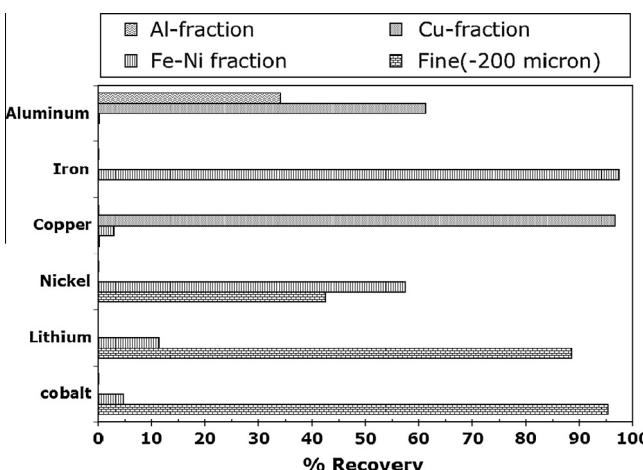


Fig. 7. Recovery of valuable metals from spent LiBs scrap by grinding, sieving, magnetic separation, and zigzag classification (Georgi-Maschlera et al., 2012).

where coarse: % of valuable metal in the coarse fraction, fine: % of valuable metal in the fine fraction, and feed: % of valuable metal in the battery scrap.

Nan et al. (2006) reported that removal of outer shell by primary crushing and sieving (20 mm for example) removes the outer iron and plastic shell and facilitate the access to the valuable material inside spent batteries. This step is also reducing the scrap volume and improving the subsequent fine grinding and magnetic separation process.

Georgi-Maschlera et al. (2012) analysis of ground spent LiBs batteries shows that coarse fraction ($+200 \mu\text{m}$) contains mainly iron, copper, and aluminum while most cobalt and lithium were concentrate in the fine fraction ($P_{80} = 100 \mu\text{m}$). As shown in Fig. 7, grinding and sieving followed by magnetic separation and zigzag classification resulted in 95% and 90% of cobalt and lithium recovery to the fine fraction ($-200 \mu\text{m}$) and about 100% of iron recovery to Fe-Ni fraction.

Granata et al. (2012) reported that after two times crushing and screening, fine electrode powder ($-1000 \mu\text{m}$) represent 49% of LiBs original mass was obtained while Lin et al. (2003) used crushing and grinding to separate LiBs casing materials and prepare powder ($-300 \mu\text{m}$) rich in cobalt and lithium to be used in membrane hydrolysis for cobalt and lithium extraction.

Shin et al. (2005) reported that fine grinding affecting the efficiency of metallurgical process by reducing the amount of leachate required for spent batteries leaching. Using coarse electrode powder ($-850 + 200 \mu\text{m}$) reduces the efficiency of cobalt leaching by 20% compared with ($-106 \mu\text{m}$) powder at the same leaching condition which requires increasing leaching agent quantity to improve the leaching process.

As mentioned earlier, even though incineration of spent LiBs removes their carbon and organics content; it significantly reduces the efficiency of subsequent hydrometallurgical process. Shin et al. (2005) reported that incineration reduces the efficiency of cobalt and lithium by 50% and 10%, respectively due to covering cobalt surface by molten alumina. According to Shin et al. (2005) fine crushing followed by sieving almost completely removed the aluminum foil from the electrode powder which subsequently reduces the hydrometallurgical steps required to extract valuable metals from leach liquor.

Recupyl process (Tedjar and Foudraz, 2010) is one of recycling processes which extensively used physical separation to safely disintegrate LiBs. In this process two crushing step at low and high speed rotary shredder was performed while the crushing system was inserted in a sealed medium filled with a mixture of CO_2 and argon. Crushing in inert gas expel oxygen and nitrogen and formed less reactive lithium carbonate. The crushed scrap was then sieved and passed through high magnetic separator and densimetric table to produce heavy-magnetic fraction consists mainly of steel used in battery casing. Light-none magnetic consist of plastics and papers, heavy – non-magnetic mainly composed of non-ferrous metals, and finally fine fraction rich in metal oxides and carbon. The fine fraction were further sieved by $500 \mu\text{m}$ sieve and separated into fine-cobalt rich fraction and coarse-copper rich fraction.

Another physicochemical separation process is mechanochemical method suggested by Saeki et al. (2004). It depends on disordering the structure of LiCoO_2 by grinding to form lithium and cobalt chlorides. Cobalt is reduced in presence of chlorine (Cl) provided by PVC which co-ground with spent batteries cathode materials. So the soluble salt can be leached by water at room temperature and separated by filtration. However, although this method is attractive it requires long grinding time to complete LiCoO_2 disordering; approximately 30 h of grinding were required to achieve 90% recovery of cobalt and lithium which makes process unattractive from economic standpoint.

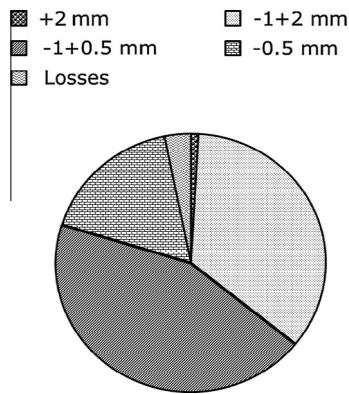


Fig. 8. Weight distribution of NiMH battery scrap after crushing and sieving (Huang et al., 2011).

5.2. Mechanical treatment of NiMH batteries

Contestabile et al. (2001) emphasized the importance of crushing and classification in increasing the efficiency of NiMH battery recycling while Shin et al. (2005) reported that two times crushing and sieving of spent NiMH batteries produced powder ($-1000\text{ }\mu\text{m}$) representing 49% of the original battery weight and reducing the weight loss of coarse fraction to 7%. It also reduces the losses during Eddy current separation to less than 4%.

Also, Kaneko et al. (1995) used crushing (-5 mm) of spent NiMH batteries followed by magnetic and wet gravity separation to separate ferrous metals and plastic and papers in order to provide powder rich of Ni and Ni-rare earth metals in order to extract them by molten salt electrolysis.

Bertuol et al. (2006) used two stages of crushing followed by two stages of magnetic separation to separate NiMH high magnetic from the non-magnetic part. The authors do not provide detailed chemical analysis of each stream in order to evaluate the separation efficiency and compare it with other results reported in the literature. As shown in Fig. 8, crushing followed by sieving concentrate most of NiMH batteries scrap in the size fraction (-1 mm), while the losses due to crushing and sieving was less than 3%. On the other hand, Fig. 9 shows that apart from copper, the valuable metals were concentrated in the ($-1+0.5\text{ mm}$) fraction followed by ($-2+1\text{ mm}$) fraction. Copper was concentrated in the (-0.5 mm) and ($-1+0.5\text{ mm}$) fractions while manganese was concentrated in the ($-1+0.5\text{ mm}$) and (-0.5 mm) fractions.

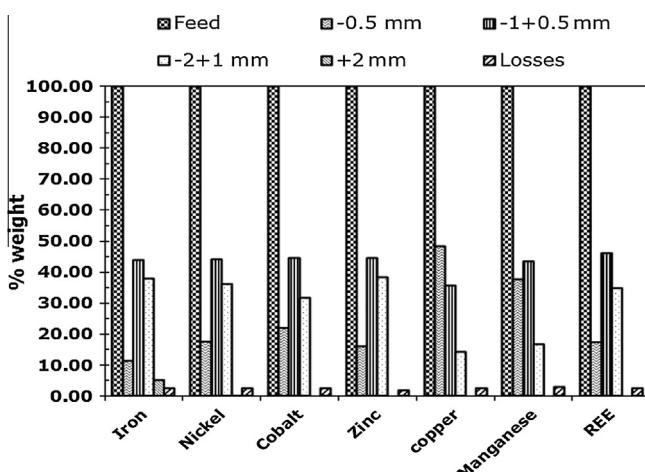


Fig. 9. Valuable metals distribution in NiMH battery scrape after crushing and sieving (Huang et al., 2011).

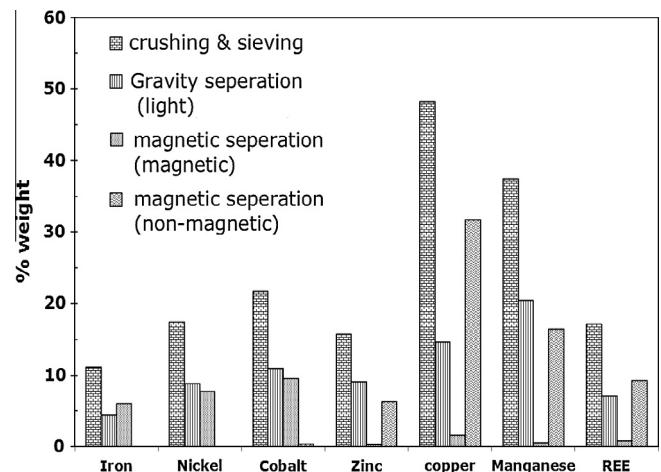


Fig. 10. Valuable metals distribution in NiMH battery scrap (-0.5 mm) fraction after crushing and sieving, gravity and magnetic separation (Huang et al., 2011).

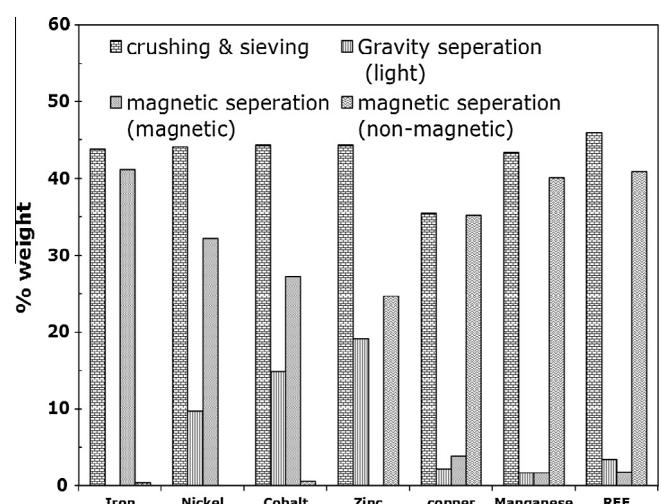


Fig. 11. Valuable metals distribution in NiMH battery scrape ($-1+0.5\text{ mm}$) fraction after crushing and sieving, gravity and magnetic separation (Huang et al., 2011).

Applying gravity separation followed by magnetic separation on the fine (-0.5 mm) and ($-1+0.5\text{ mm}$) fractions (Fig. 10) shows that copper concentrated in the non-magnetic followed by light gravity fraction while manganese, zinc and REE were concentrated in the light gravity fraction followed by non-magnetic fraction. Cobalt, nickel, and iron were almost evenly divided between the light and magnetic fractions. Fig. 11 shows that most copper, manganese, zinc, and REE were concentrated in the non-magnetic fraction while most of cobalt and nickel were concentrated in the magnetic fraction. However, about 15–20% of cobalt, nickel, and zinc were reported to the light fraction of gravity separation. On the other hand almost 100% of iron was reported to magnetic fraction.

5.3. Mechanical treatment of emerging batteries types (polymer electrolyte, button like batteries)

Cardarelli and Dubi (2007) used wet grinding ($-1000\text{ }\mu\text{m}$) to liberate LMPB components (metal lithium, solid gel electrolyte, polymer electrolyte, lithium vanadium oxide powder, carbon, and aluminum foil) using a rotary cutting mill with liquid nitrogen in order to reduce the reactivity of spent cells. They then used hydrocyclone and centrifuge to remove insoluble solid from spent

LMPB-sulfuric acid solution before applying pressure filtration to prepare mother liquor for the recovery of vanadium, lithium, and aluminum from spent LMPB.

Heng et al. (1988) used crushing and grinding to liberate the components (electrode and case materials) of small and button like batteries. They used disintegration method consists of crushing spent batteries by impact crusher followed by roasting (800 °C) to recover the volatile materials. Then the remaining scrap was sieved into three fractions: coarse (+20 mm), medium (−20 + 1 mm), and fine (−1 mm). The medium fraction were crushed in impact crusher and sieved for coarse (+1 mm) and fine (−1 mm) fractions. The coarse fraction (+1 mm) from the second crushing step were crushed by rod mill and sieved into two fractions, coarse (+1 mm) and fine (−1 mm). The coarse fraction from the third crushing step was subjected to magnetic separation were iron-rich fraction is separated from Cu-rich fraction. Finally, they got fine fraction (−1 mm) rich of manganese, zinc, and silver by combining the fine fractions, Cu-rich fraction (+1 mm), and iron-rich coarse fraction (+20 mm).

6. Economics of battery recycling

In order to evaluate the economic advantage of using mechanical processing in battery scrap recycling, a comparison between two scenarios were conducted; the first scenario is when battery

scrap is firstly incinerated then extracting valuable metals by hydrometallurgy, while the second scenario consists of using crushing and sieving to classify the scrap to coarse and fine part and only the coarse part is smelted while the valuable metals were extracted from the fine part by hydrometallurgy.

As shown in Fig. 12, when pyrometallurgy-hydrometallurgical route was used, a total of 0.851 ton per each ton of LiBs scrap was lost; most of the losses occurred in pyrometallurgical process where plastics, electrolyte, and some non-recyclable metals such as lithium were either evaporated or slagged. On the other hand, the total losses in mechanical processing-pyrometallurgy-hydrometallurgy route were just 0.629 ton/ton scrap (i.e. 26% smaller).

In order to compare the profitability of each route, assume that the cost of smelting and hydrometallurgy is X\$/ton and Y\$/ton, respectively. The cost of crushing and sieving (C&S) was calculated based on the bond work index of a hard rock (iron ore) which is 20 kW h/ton (McNab et al., 2009). So, if the cost of each kW h is \$1 and the efficiency of crushing is 80%, the cost for each ton scrap will be \$25/ton ($1.25 * 20 * 1$). On the other hand, the cost of Eddy current (EC) and/or Electrostatic (ES) separation was also estimated based on the requirement of upgrading 1 ton of iron ore which is approximately 5 kW h/ton (McNab et al., 2009). Therefore the cost of EC/ES is 6.25 \$/ton assuming 80% efficiency. The revenue was calculated using current price of metals as shown in Table 1 (The global source of minerals prices, 2012). The fifth column in Table 1 shows the weight factor of each metal in

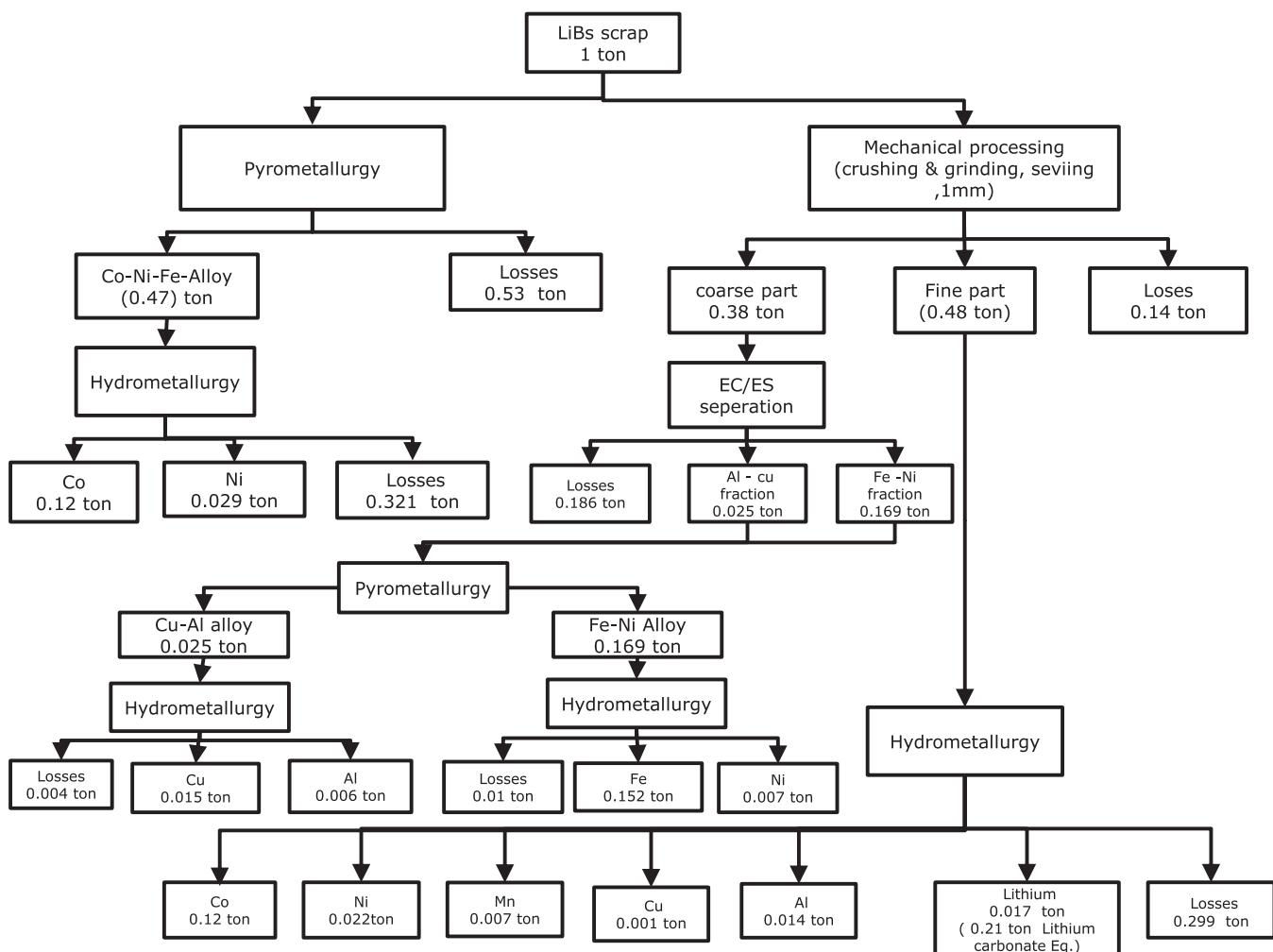


Fig. 12. LiBs battery recycling by mechanical processing, pyrometallurgy and hydrometallurgy.

Table 1

The price of metals in LiBs scrap (\$/ton).

Metal	Price (\$/ton)	Tons recovered (ton/ton scrap)		Hydro. factor	Revenue (\$/ton scrap)	
		Pyro.-hydro.	Mech.-pyro.-hydro.		Pyro.-hydro.	Mech.-pyro.-hydro.
Co	25,000	0.12	0.12	0.17	3000	3000
Cu	5000		0.016	0.13		80
NI	15,000	0.029	0.029	0.17	435	435
Al	1600		0.02	0.13		32
Mn	3000		0.007	0.17		21
Li_2CO_3	4000		0.21	0.17		840
Fe	200		0.152	0.08		30.4
Total					3435	4438.4

Table 2

The cost of recycling process by each of recycling route.

Route	Cost (\$/ton scrap)				Total cost (\$/ton)	Total revenue (\$/ton)
	C&S	EC/ES	Hydro.	Pyro.		
Mech. pro.-pyro.-hydro.	25	2.4	0.501Y	0.194X	$27.4 + 0.501Y + 0.194X$	4438.4
Pyro.-hydro.	–	–	0.47Y	X	$0.47Y + X$	3435

Table 3

Simulation results of different scenarios for hydrometallurgy (Y) and pyrometallurgy (X) cost.

Cost (\$/ton)	Profit (\$/ton)		Difference (1–2)	
	X	Y	Pyro.-hydro. (1)	Mech.-pyro.-hydro. (2)
100	1000	3805.0	2485.3	–1319.7
250	1000	3655.0	2531.3	–1123.7
500	1000	3405.0	2608.1	–796.9
1000	1000	2905.0	2761.6	–143.4
2000	1000	1905.0	3068.6	1163.6
3000	1000	905.0	3375.6	2470.6
4000	1000	–95.0	3682.6	3777.6
1000	500	2670.0	2879.3	209.3
1000	1000	2905.0	2761.6	–143.4
1000	2000	3375.0	2526.1	–848.9
1000	3000	3845.0	2290.7	–1554.3
1000	4000	4315.0	2055.2	–2259.8
1000	5000	4785.0	1819.7	–2965.3

Using different scenarios for the price of both hydrometallurgical and pyrometallurgical processes as shown in **Table 3**, the profitability of each processing route can be compared. As shown in the table, pyrometallurgical–hydrometallurgical route is more profitable when the cost of pyrometallurgy is low. On the other hand, the mechanical processing–pyrometallurgical–hydrometallurgical route was more profitable at low cost hydrometallurgy up to half of the pyrometallurgical process cost

As mentioned earlier, [Shin et al. \(2005\)](#) reported that incineration reduces the efficiency of cobalt and lithium extraction by hydrometallurgy by 50% and 10%, respectively. So, **Table 4** shows a new simulation results where data were recalculated to reflect the reduction in revenue if pyrometallurgical and hydrometallurgical route were employed. It is shown that mechanical processing–hydrometallurgical–pyrometallurgical route becomes more profitable even when the cost of hydrometallurgy is three times higher.

7. Proposed flowsheet for recycling mixed LiBs and NiMH batteries

The importance of using mechanical processing as a prerequisite for more expensive hydrometallurgical and pyrometallurgical processes was highlighted in previous discussions. Therefore, we proposed a flowsheet ([Fig. 13](#)) which is a combination of minerals processing operations; this will ensure proper liberation of battery scrap valuable metals in order to separate as much as possible of battery scrap constituents to reduce the interference of these impurities with hydrometallurgical/pyrometallurgical processes used in the final purification process.

The first step is to deactivate the battery scrap by submerging in liquid nitrogen or inert gas to avoid any risks of fire or releasing toxic gas by interaction with atmosphere. Then the scrap will be subjected to primary crushing to open the casing materials and liberate electrode part. [Ruffino et al. \(2011\)](#) reported that different battery shape has different resistance to crushing and grinding. this problem can be overcome by crushing the mixed stream with more than one stage of crushing followed by screening or by using primary crusher equipped with internal screen to ensure that only scrap pieces under specific size will pass to the secondary crushing stage.

The crushed scrap will then be subjected to primary dry screening to separate large pieces of scrap from the fine electrodeal

Table 4

Modified simulation results of different scenarios for hydrometallurgy (Y) and pyrometallurgy (X) cost.

Cost (\$/ton)	Profit (\$/ton)		Difference (1–2)	
	X	Y	Pyro.-hydro. (1)	Mech.-pyro.-hydro. (2)
100	1000	2305.0	3236.8	931.8
250	1000	2155.0	3282.8	1127.8
500	1000	1905.0	3359.6	1454.6
1000	1000	1405.0	3513.1	2108.1
2000	1000	405.0	3820.1	3415.1
3000	1000	–595.0	4127.1	4722.1
4000	1000	–1595.0	4434.1	6029.1
1000	500	1170.0	3630.8	2460.8
1000	1000	1405.0	3513.1	2108.1
1000	2000	1875.0	3277.6	1402.6
1000	3000	2345.0	3042.2	697.2
1000	4000	2815.0	2806.7	–8.3
1000	5000	3285.0	2571.2	–713.8

hydrometallurgical purification process where the metals of higher number are those requires more purification steps and therefore higher cost. A summary of these calculations is given in **Table 2**. However, it should be clear that these numbers are for comparison only since they based on the assumption of 100% recovery of metals without taking into account other costs which occur during recycling process.

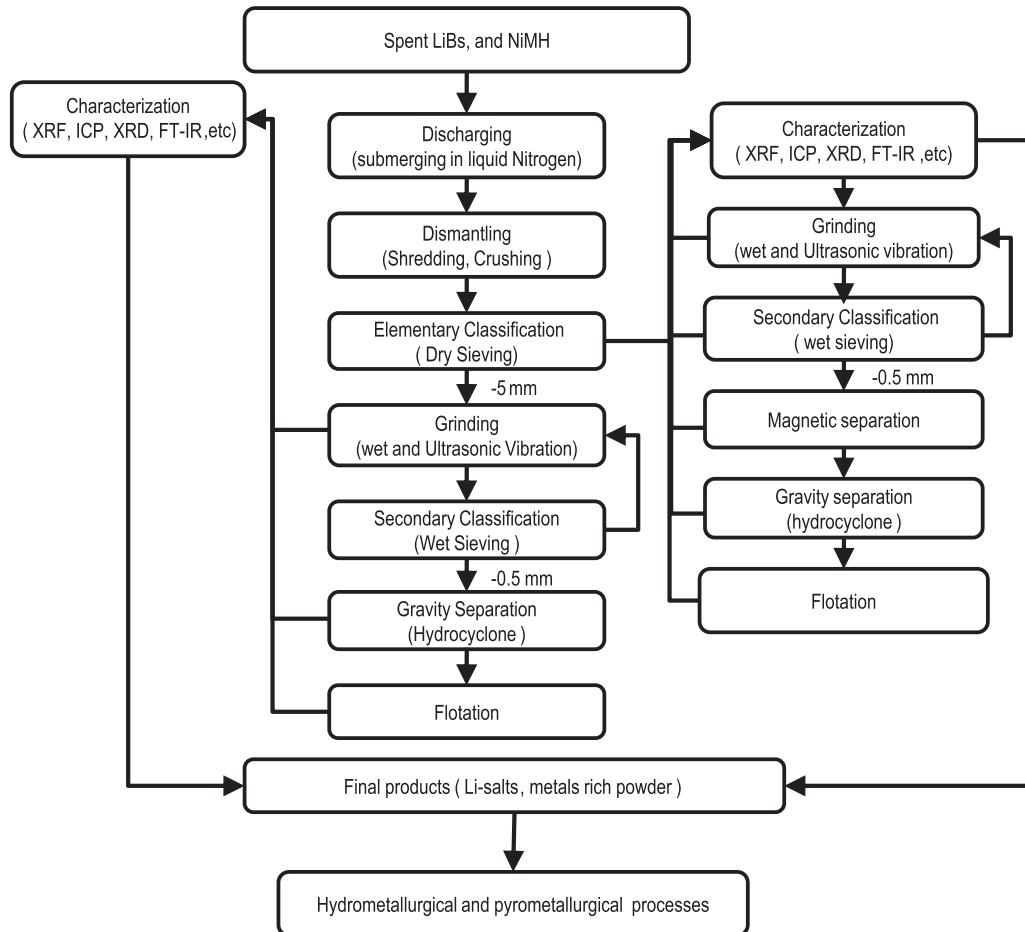


Fig. 13. Proposed flowsheet for recycling mixed LiBs and NiMH batteries scrap.

materials. Because of some electrodal materials may still adhered to the coarse scrap (+5 mm), the later will be subjected to wet grinding with ultrasonic vibration to scrub fine particles adhered to the coarser scrap pieces. In this stage NMP solvent as suggested by Castillo et al. (2002) may be used. Crushing followed by ultrasonic vibration were employed by Li et al. (2009) to facilitate the separation of electrodal materials from their supported substrate which improved the recovery of Co and Li from LiBs scrap. Magnetic separation was then applied to separate the magnetic from non-magnetic materials. Electrostatic separation may also be used to separate the conducting from none conducting materials. The -5 mm scrap will be subjected to a second stage of wet fine grinding followed by sieving. Gravity and electrostatic separation may be employed to separate the remaining casing and electrodal substrate materials.

On the other hand, the fine particles -0.5 mm will be subjected to gravity separation (shaking table) and classification (hydrocyclone) to separate fine and light particles from the heavier and larger one. The fine fraction may also be separated to coarse and fine fractions which can be treated separately. Ito et al. (2010) separate anode and cathode materials of NiMH battery by grinding to $-75 \mu\text{m}$ then classify the fine particles by hydrocyclone. The final stage in this upgrading flowsheet is to use collectorless flotation in order to separate fine hydrophobic particles mainly carbon which cannot be separated by previous upgrading steps. In order to ensure no new chemicals is introduced to the system, only pH modifiers such as sodium hydroxide or sodium carbonate can be

used. The fine powder is then dewatered, filtered, and dried. Hydrometallurgical or pyrometallurgical processed to produce alloys or pure metal oxides.

8. Summary and conclusions

Based on previous discussion, the following conclusions can be drawn:

1. LiBs and NiMH batteries currently share more than 80% of rechargeable batteries market. Production of these cells is expected to increase rapidly due to the soaring price of oil and gas which increases interest in renewable energy as well as the introduction of HV, and EV which used secondary batteries as an effective energy storage device.
2. Safe disposal of these batteries at their end life is an environmental necessity since some of their components are difficult to degrade and dispose them with municipal waste may pollute the soil and underground water and contaminated the air by releasing toxic gases if they incinerated. Also, the recent surge in minerals price turned these types of secondary batteries as a cheaper source of valuable metals. The main metals in LiBs scrap are cobalt, nickel, lithium, copper, manganese, and iron/steel while NiMH batteries contain nickel, cobalt, zinc, manganese, and iron/steel as well as REE such as lanthanum, neodymium, cerium, praseodymium, and samarium. Therefore, the development of an efficient recycling scheme to recover the

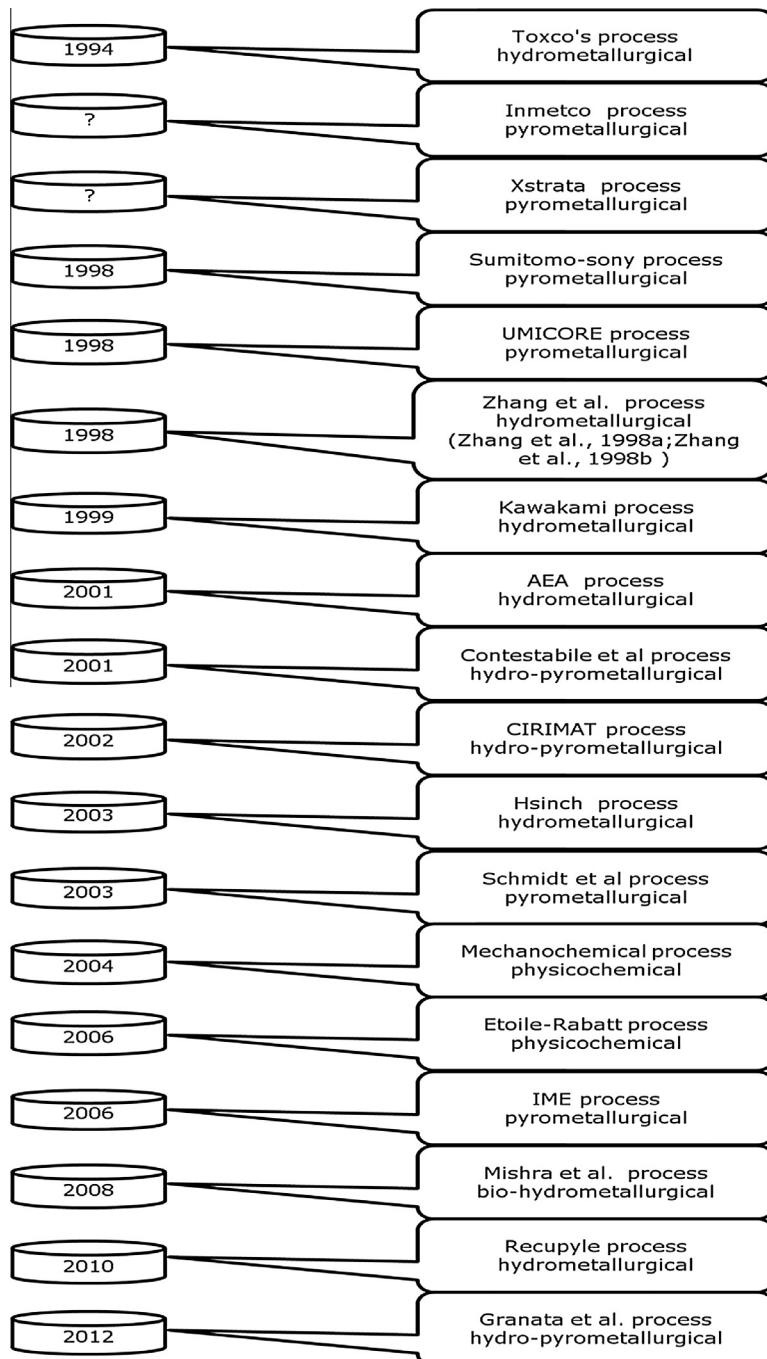


Fig. 14. Timeline of the development of LiBs and NiMH battery recycling processes.

valuable parts and safely dispose the harmful one is a necessity. The challenge, however, is how to recover all the valuable metals without sacrificing the economics of recycling process.

3. Several LiBs and NiMH batteries recycling processes have been developed in recent years. The time line of their developments is shown in Fig. 14. However, the major drawbacks of these recycling processes are the losses of some of valuable parts since these recycling processes were not originally developed for LiBs and NiMH batteries. Also, some of these processes are expensive and designed for specific types of batteries which ignore contamination of recycling stream with impurities and other type of batteries.

4. Using minerals processing operations such as grinding, sieving, magnetic, electrostatic, and gravity separations to liberate batteries electrode materials and concentrate valuable metals is critical step in any recycling process due to their simplicity, efficiency, flexibility, and high throughput. Applying these processes will reduce the volume of LiBs and NiMH batteries, liberate their valuables, reduce the need for leachate purification in hydrometallurgical process, and facilitates the decomposing of battery electrolyte. However, previous discussions showed that using a single process/stage of these minerals processing operations does not fully liberate the valuable materials from battery scrap. Therefore, a flowsheet to recycle mixed stream LiBs, and NiMH battery scrap was proposed.

Acknowledgments

The authors would like to thank Japan Society for Promotion of Science (JSPS) for their generous fellowship to the first author. Also, Dr. Salah sincerely thanks Prof. Nakamura and his laboratory staff for their warm welcome and support during his stay in the Institute of Multidisciplinary research for advanced materials (IMRAM), Tohoku University, Japan.

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